

# Theoretical and computational study of high pressure structures in barium

Stewart K. Reed and Graeme J. Ackland

Department of Physics and Astronomy, The University of Edinburgh  
Edinburgh, EH9 3JZ, Scotland, United Kingdom

Recent high pressure work has suggested that elemental barium forms a high pressure self-hosting structure (Ba IV) involving two ‘types’ of barium atom. Uniquely among reported elemental structures it cannot be described by a single crystalline lattice, instead involving two interpenetrating incommensurate lattices. In this letter we report pseudopotential calculations demonstrating the stability and the potentially disordered nature of the ‘guest’ structure. Using band structures and nearly-free electron theory we relate the appearance of Ba IV to an instability in the close-packed structure, demonstrate that it has a zero energy vibrational mode, and speculate about the structure’s stability in other divalent elements.

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The high pressure structures of the alkaline earth metals show an unusual trend in going from apparently close packed structures at low pressure to more complex open structures at higher pressure. This counterintuitive behavior arises from transfer of electrons from free-electron like s-bands to more directional d-bands.

Barium has a number of still more unusual features. It adopts the body-centered-cubic (bcc) structure at zero pressure (conventionally denoted phase I). Under 5.5 GPa of pressure it transforms to phase II with a hexagonal-close-packed structure (hcp). At 12.6 GPa it transforms into the complex phase IV and then back to hcp (phase V) at 45 GPa. This last phase is observed experimentally up to at least 90 GPa. Until recently all attempts to solve the phase IV structure have failed.

Nelmes *et al* [1] have now shown that Ba IV has a complicated structure consisting of two interpenetrating but incommensurate structures: a tetragonal ‘host’ with ‘guest’ chains in channels along the *c*-axis of the host. Although they share the same *a* and *b* parameters the guest and host lattices are incommensurate in the *c*-axis. Viewed along *c*, the eight atoms in the host unit cell are arranged in an octagon but with atoms at alternating heights. The guest chains pass through the middle of these octagons, and a combination of diffuse scattering and Bragg peaks suggests regions of both order and disorder between the chains. Figure 1 illustrates the unit cells and describes how Ba IV splits up in distinct ‘subphases’ depending on the registry of adjacent chains.

An unusual feature of the hcp phase is the strong pressure dependence shown by the *c/a* ratio in phase II: it falls to  $\sim 1.50$  at the II-IV transition, so far below the ideal value (1.633) that the structure can hardly be regarded as close packed. In phase V however, which is also hcp, the reported *c/a* ratio is almost pressure independent at  $\sim 1.58$  [2].

In this paper we present total energy calculations on the observed and other possible structures. These enable us to probe experimentally unobservable quantities such as the energy barrier to moving the chains and

whether there is an isostructural II-V phase transition ‘hidden’ in the range of pressures where Ba IV is more stable. Dealing with the incommensurate double-lattice provides a unique challenge for simulations based on periodic boundary conditions.

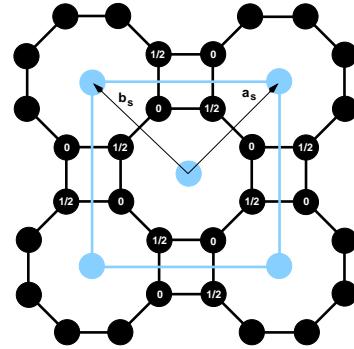


FIG. 1. Schematic representation of the Ba IV structure. The host atoms (dark symbols) with chains of guest atoms (light symbols) are projected on to the *ab*-plane. The host atoms are labeled with their *z* coordinates. The arrows labelled  $a_s$  and  $b_s$  are projections of the supercell vectors used in the calculations. At 12.1 GPa the host cell has dimensions  $a_{host} = b_{host} = 8.42\text{\AA}$  and  $c_{host} = 4.74\text{\AA}$ . Full description of the observed guest atoms involves three unit cells. One is partially disordered and tetragonal with the same *a* and *b* as the host structure but with  $c_{guest,t} = 3.41\text{\AA}$ . On ordering, the guest structure can undergo a monoclinic distortion to one of four similar cells, related by 90° rotations about the tetragonal axis, with  $a_{guest,m} = 8.46\text{\AA}$ ,  $b_{guest,m} = a_{host}$ ,  $c_{guest,m} = 3.43\text{\AA}$  and  $\beta_{guest,m} = 96.15^\circ$ . This corresponds to displacement of atoms in adjacent chains by  $0.47\text{\AA}$  along *c*.

The calculations are done using the *ab initio* total-energy density-functional-theory [3–5] plane-wave ultrasoft pseudopotential method [6,10] which is well documented elsewhere. The generalized gradient approximation [7] was used for exchange and correlation. The plane wave basis is cut off at 350 eV which is sufficient to con-

verge total energies to better than 0.1 meV per atom. Sampling of the reciprocal space uses symmetry-reduced k-point sets [8] converged to 0.1 meV per atom. Eight valence electrons per atom are treated explicitly. We calculate the total energies for the bcc, fcc, hcp and Ba IV structures. In all cases the enthalpy is minimized with respect to ionic and unit cell degrees of freedom under hydrostatic pressure using Hellman-Feynman forces and analytic stresses with Pulay corrections [9].

Plane wave calculations are done with periodic boundary conditions, but it is impossible to model an incommensurate structure exactly using a supercell. Hence Ba IV was approximated by a similar commensurate structure: pseudo-Ba IV comprises a monoclinic supercell (s) containing eight host and three guest atoms with  $a_s = \frac{1}{2}(b_{host} + a_{host}) + \frac{1}{2}c_{host}$ ,  $b_s = \frac{1}{2}(b_{host} - a_{host}) + \frac{1}{2}c_{host}$  and  $c_s = 2c_{host}$ . Before relaxation three guest atoms were evenly distributed along the  $c$ -axis from the origin. This arrangement gives a  $c_{host}$  to  $c_{guest}$  ratio of 1.5 compared to experimental value of about 1.39. Furthermore, since  $a_s$  and  $b_s$  both contain a component in the  $c_{host}$  direction the neighboring columns of guest atoms are displaced in the  $c_{host}$  direction with respect to each other more than is seen experimentally [11]. The total energy for this cell will represent an upper bound on the energy of incommensurate Ba IV.

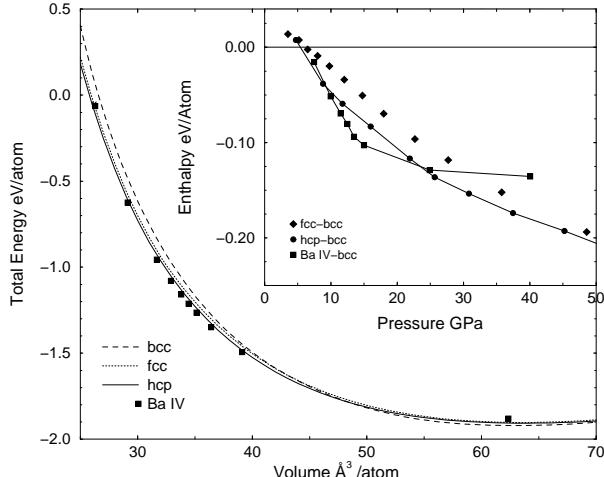


FIG. 2. Graph of energy against volume for various phases. At larger volumes bcc has the lowest energy, while hcp is lower below  $\sim 48 \pm 2 \text{ Å}^3$ . The inset shows the differences in enthalpy between the hcp, BaIV and fcc with reference to that of bcc. The calculated Ba IV data is shifted by  $-0.065 \text{ eV}$  (see text) to account for the incommensurability.

The results of the calculations are shown in figure 2. The energy differences between the bcc, fcc and hcp structures are small but they are nonetheless greater than the accuracy of the calculations. In agreement with experiment, bcc is the favored structure at ambient pressure with a phase transition to hcp at around 5 GPa.

The pseudo-Ba IV phase energy is close to the hcp curve, moving away at low and high pressure: evidence of the reentrant nature of the hcp phase.

The overestimate of the energy in calculating pseudo-Ba IV rather than incommensurate Ba IV can be approximated by a simple elastic model: assume that to form pseudo-Ba IV the Ba IV guest lattice has been independently compressed and the host lattice expanded until the experimentally measured ratio  $c_{host}/c_{guest} = 1.39$  [1] reaches the commensurate value of the supercell: 1.5.

By measuring the stress  $\sigma_{33}$  of the commensurate cell under uniaxial compression  $\epsilon_{33}$  and assuming that guest and host lattices separately have the same elastic constant  $C_{33}$ , linear elasticity yields a strain energy of:

$$\Delta E = \frac{V}{4} C_{33} [1 - 2c_{host}/3c_{guest}]^2$$

The composite elastic modulus  $C_{33}$  can be measured by a finite strain [12] calculation, taking a pressure independent  $C_{33} = 150 \text{ GPa}$  gives the energy shift  $\Delta E = 0.065 \text{ eV/atom}$  which is included in figure 2. The Ba IV enthalpy lies below hcp between 9.5 GPa and 23 GPa, in reasonable agreement with experiment. The exact transition pressures are sensitive to this correction.

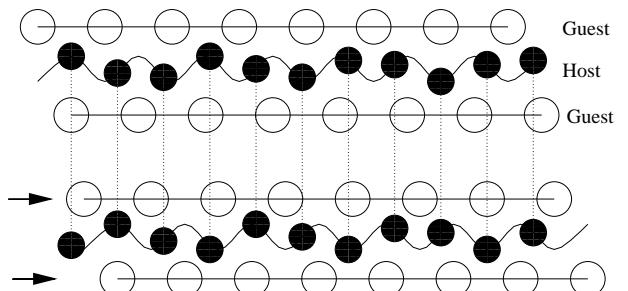


FIG. 3. In an incommensurate structure, guest atoms occur at all possible heights in the host unit cell. The guest-host interactions could induce a modulation with period  $c_{guest}$  in the host which would yield an indirect chain-chain coupling (upper figure, with the host displacements much exaggerated). Since all local registries are observed somewhere along the chain, the energy change due to a vibrational mode displacing the guest chains along their length with respect to the host is exactly zero (lower figure). The host modulation would move with the guest atoms holding adjacent chains in registry with one another.

The offset of the origin of the two lattices must be defined for commensurate structures: we used a range of origin offsets and found that the energies varied between them by less than  $0.001 \text{ eV/atom}$  and the relaxed volumes by less than  $0.02\%$  [13]. This shows that no position of the guests is more favorable than any other which means that the guests can be at any height with respect to the hosts without there being an ‘energy penalty’ to pay. Thus the  $c_{guest}$  is determined by the packing along the chain rather than host-guest interactions. In the fully incommensurate case this would lead to a zero frequency phonon mode, or phason (figure 3).

The calculated  $c/a$  ratio was 0.58 as compared with experiment  $c_{host}/a_{host}$  value of 0.56. This can be explained by the elastic model: 0.2 more guest atoms have been forced into the cell than would be ideal, applying a stress on the host. The host cell therefore responds by expanding in the  $c$ -direction.

Moreover, hcp calculations show a plateau in the Fermi energy between 18 GPa and 43 GPa resulting from a peak in the density of states. Typically, this would lead to a Jahn-Teller type instability of hcp.

Recent studies [2,14] of the two hcp phases have shown a dramatic decrease in the  $c/a$  ratio in phase II with increasing pressure. In phase V it is noted that the ratio is almost constant, slightly less than ideal. Experimentally it is impossible to get data between 12 GPa and 45 GPa because hcp is unstable in this region; it is nevertheless possible to do calculations.

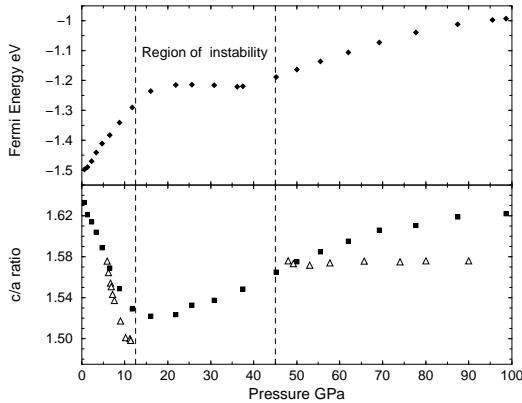


FIG. 4. Pressure dependence of the Fermi energy (top) and  $c/a$  ratio (bottom) for hcp Ba, from constant (hydrostatic) pressure calculations. The open triangles are experimental data taken by Takemura [2].

As figure 4 illustrates our  $c/a$  results initially agree very well with experiments and remain in good agreement up to the phase transition. In the experimentally inaccessible region we find a steady increase in  $c/a$ , and decrease in volume until once again good agreement is obtained when the hcp phase is again observed at 45 GPa. Thus we have demonstrated that phase II and phase V are actually the same phase, with the variation in  $c/a$  due to a continuous transfer of electrons from  $s$  to  $d$ . Zeng et al [15] calculated the  $c/a$  ratio using the linear muffin-tin orbital method for electrons in a variety of different configurations. They found that, at 5.7 GPa near the onset of phase II, a better fit to the experiments was obtained if they included  $d$ -orbitals as well as  $s$ - and  $p$ -orbitals. They attribute the variable  $c/a$  ratio to strong  $s \rightarrow d$  transfer across phase II, but report a much smaller effect in phase V.

To interpret these results, we consider packing of hard spheres and the nearly free electron model. [16]. As the host and guest cells are incommensurate the guest atoms must be able to take any (every) height with respect

to the host cell. In the packing model this implies that the guest atoms must be able to pass through the octagonal host rings. With hard sphere atoms this would mean either the host atoms cannot be in mutual contact or the guest atoms must be smaller than the hosts. Even then, the packing fraction is 0.56 whereas, at the II-IV transition the hcp phase II has a packing fraction of 0.68. This suggests that efficient packing is insufficient to understand the structure.

In the electron gas/pseudopotential perturbation theory model of Heine and Hafner [16], screening of the nuclear charges gives rise to an oscillatory effective pair potential between atoms. The favored crystal structure is determined by this pair potential, and for Ba the high pressure close packed structures have atoms at unfavorable separations, near maxima in the pair potential [15]. Thus the 'ideal' hcp structure is unstable with respect to splitting the shell of 12 nearest neighbors into 6 and 6 by altering the  $c/a$  ratio.

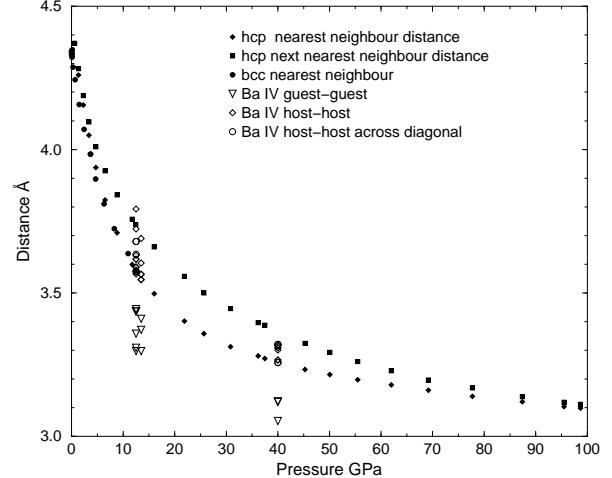


FIG. 5. Observed bond lengths as a function of pressure in hcp, bcc and Ba IV structures. The Ba IV interhost distances are similar to the neighbor distances in hcp, which themselves are a continuation of the bcc distances. The Ba IV guest separation is consistently lower. The shortest possible guest-host distance is half the distance across the host octagon, which is slightly more than the smallest guest-guest spacing. Hence the guest atom is more compressed than the host.

Since the potential depends only on interatomic spacings, competing structures will have neighbor separations similar to the optimally distorted hcp. In our calculations (figure 5) we find that bcc and hcp have approximately the same nearest-neighbor distance at room temperature. As the pressure increases the hcp nearest neighbor distance splits into two due to the non-ideal  $c/a$  ratio. At the II-IV transition the intra-guest distance is 3.41 Å, and the shortest intra-host distance is 3.43 Å. These distances are close to the nearest neighbor distances in hcp (3.46 Å).

As a result of the incommensurability, a range of host-guest separations nearest-neighbor distances should occur. The similarity of bondlengths (figure 5) to those of hcp shows that Ba IV structure represents another way of arranging the atoms such that they lie in a minima of the screened electrostatic potential.

An alternate view of the nearly free electron picture [17] is that the energy is lowered by perturbation of states near the Fermi surface: this favors structures which have Brillouin zone faces close to the Fermi vector. Incommensurate Ba IV has two Brillouin zones with the (220), (211)<sub>host</sub> and (111)<sub>guest</sub> facets of the first zones close to the divalent free electron Fermi vector [18].

In sum, the total energy pseudopotential method gives an excellent description of the experimentally observed high pressure phase diagram for barium, including the complex guest-host structure Ba IV. Although one can not represent the full incommensurate structure in a supercell calculation, the energy of an equivalent commensurate pseudo-Ba IV structure is close to that of hcp: treating the mismatch using linear elasticity shows that incommensurate Ba IV has a region of stability.

Calculations involving moving the guest chains within their channels, show the interchain interactions of the guest atoms to be very weak, probably mediated by elastic strain in the host. Based on this we propose that the tetragonal phase [1] is metastable. Weak interactions mediated by strain in the host lead to ordering at low T. The least favored arrangement in terms of strain would be to have all guest atoms simultaneously coplanar, and so each chain is displaced relative to its neighbors leading to the monoclinic phase [19].

Ba IV an unusual example of a stable elemental structure with two inequivalent atomic sites. Pressurization of barium proceeds by transfer of electrons from low energy, extended s-states to higher energy, more localized d-states. The hcp structure represents one method of achieving intermediate *sd* bonding: hybridized orbitals with all atoms equivalent. Ba IV offers another mechanism, with a division between guest atoms containing more d-like character and host atoms having more s-like behavior: a projection of the Kohn-Sham wavefunctions onto atom centered orbitals shows *s* – *d* transfer in all structures and a 20% greater *s*-character on the host atoms compared to the guest atoms in the region of Ba IV stability. The *p* and *d*-character discrepancy was less pronounced, suggestive of a transfer from *s* to more free-electron like behavior. The larger number of electrons ‘localized’ on the host atoms is consistent with their apparently smaller size. Thus Ba IV can be regarded as an intermetallic compound, in which both components are actually the same element.

The free electron theory suggests that Ba IV will be a competitor with hcp as a high pressure phase not just in Ba, but in other materials with similar valence electron density and *s* → *d* electron transfer. Moreover the reduced size of the *d*-like atom will lead to faster diffusion and lower melting points at high pressures.

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